

Synthesis and a Preliminary Characterization of Poly(Propylene)imine Hexadecylamine Dendrimer (DAB-Am-16) Modified with Methyl Acrylate

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Authors' contributions

This work was carried out in collaboration between all authors. Author LLP synthesized the material and made its dielectric characterization. Author TFSS made an analysis of vibrational spectroscopy. Author RSL performed nuclear magnetic resonance analysis in the solid state. Author LM made thermogravimetric analysis. Author UOB made the analysis of scanning electron microscopy and author NLD revised the first version of the manuscript. Author DRC collaborated with the experiments and wrote the paper. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

This paper describes the reaction of a Poly(propylene)imine hexadecylamine dendrimer (DAB-Am-16) with methyl acrylate. The modified dendrimer obtained (DKMA) was characterized by vibrational spectroscopy, nuclear resonance magnetic (¹³C), thermogravimetry and scanning electron microscopy. The dielectric properties of DKMA were studied in a temperature range of -40 to 100°C varying the frequency from 10 to 1000 KHz. A relative thermal stability was found for DKMA. The modified dendrimer

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behaved as an organic insulating ($\epsilon' = 5.1$). The synthesis performed at basic medium results in a corresponding change in the conformational property of the precursor. The electron microscopy indicated that the dendrimer presented a modified collapsed shape, expected by the proposed route of synthesis.

Keywords: Dendrimer; methyl acrylate; thermal analysis; dielectric properties; synthesis.

1. INTRODUCTION

The term Dendrimers [1], comes from the Greek word “dendron” (tree) and “meros” (parts), thus referring to the typical tree-like appearance of these compounds. Dendrimers are nanometer-dimensional monodispersed macromolecules, highly branched and spherical, prepared by interactive synthesis methods. A wide variety of synthesized dendrimers are described in numerous reviews and articles [2-7] in all fields of knowledge.

The dendrimers are derived from AB_n monomers (where $n \geq 2$ - usually equal to 2 and 3) and have three distinct structural features [8]:

- i. Nucleus: central part of the dendrimer;
- ii. Branches or arms: repeating units that form the generations;
- iii. Terminal functional groups: are the sites located at the end of the macromolecule.

The peripheral groups and the branching units are called dendrons or informally known as “wedges”. Since the first studies, successfully conducted around the 1980s [9,10], there has been an astounding interest in dendrimers, particularly since the 1990s.

Dendrimer studies cover various areas, as for instance theoretical, synthesis, characterization of structures, properties and studies on its potential applications.

Currently, there is a continuous effort to improve the efficiency and cost decrease in these macromolecules' synthesis. These materials belong to a new class of polymers with structures that greatly differ from the traditional linear polymers, and are constructed from monomers called AB [11]. The dendrimers can be prepared with high structural regularity and controlled molecular weights, where the macromolecules consisting of a central polyfunctional core are covalently bonded to layers of repeating units (generations) and to terminal functional groups. These are interdependent units and form a single molecular shape, hence rendering intrinsic properties to these molecules, such as high solubility and low viscosity [6]. There are two dendrimer synthesis routes, the convergent [12] and divergent route [13]. In the divergent method, the branching units are connected one by one, multiplying the number of peripheral groups. The convergent method follows the opposite route, the skeleton is built step by step, starting from the end groups toward the inner ones and then connected to the molecule core to yield the complete dendrimer. Usually, in the dendrimer synthesis using the convergent route, group A of monomer AB_n has to be protected or requires activation to prevent a premature reaction with group B.

Currently, the diverging route is able to produce kilograms of high-generation dendrimers, and only two classes of dendrimers, namely Poly (amido)amine (PAMAM) and poly(propylene)imine (PPI) are currently provided commercially.

Since the first successful synthesis of symmetrically branched dendrimers, this class of polymer has received considerable interest due to their wide range of potential applications, such as micelles [14,15] and the encapsulation of substances [16], such as liquid crystals [17,18] in electroanalysis [19,20], as sensors [21,22], electroluminescent devices [23,24], catalysts [25,26] and support for organic substrates [27,28] and others [29-31]. Of these applications, the most discussed ones and the reason for a large number of patents are those in which the dendrimers are used as drug carrier agents [32,33]. The rigid spheroidal architectures of these molecules lead to different properties, such as; low viscosity, high solubility and miscibility, high reactivity in the terminal chains.

The wide applicability of dendrimers is due to its structure and components, for example, third generation (G-3) poly(propylene)imine hexadecylamine Dendrimer (DAB-Am-16) have peripheral groups in their structure, consisting of sixteen NH₂ groups. These NH₂ groups are susceptible to further reactions, thus making them extremely versatile materials under different synthesis.

With the intention to investigate the afore mentioned properties of the dendrimers, the present work studies some of the properties of DAB-Am-16 (G3) modified with methyl acrylate, considering that the electrical behavior of these new materials is not described in the literature.

2. EXPERIMENTALS

Poly(propylene)imine Hexadecylamine Dendrimer was purchased from Sigma Aldrich and used without any further purification. The deionized water (Milli-Q Gradient system from Millipore) was used. All the other reagents were analytical grade (Merck) and used without any further purification.

2.1 Preparation of the Modified DAB-Am-16

The material was initially prepared according to the following procedure: 1.0g of DAB-Am-16 and 0.84g of methyl acrylate were added to a volumetric flask containing 25mL of tetrahydrofuran (THF), under stirring until solubilization. The mixture was then cooled in an ice bath at 0°C for 30 min. Next, the bath was removed and a KOH solution (1.0x10⁻³ mol mL⁻¹) was added. The mixture was kept overnight in repose. Next, the mixture was lyophilized and the solid obtained was dissolved in methanol. This step was repeated one more time, and then the compound was washed with 10mL of a hydroalcolic mixture (60%). The dried product was stored in a desiccator under vacuum. The compound obtained was described as DKMA.

2.2 Methods of Characterization of Modified DAB-Am-16

2.2.1 Vibrational spectroscopy (FT-IR)

A preliminary characterization of DKMA was performed by spectroscopy in the infrared region and by dielectric spectroscopy. The infrared spectra were obtained using a Nicolet 5DXB FT-IR spectrophotometer. In this case the sample was mixed with KBr in the mass proportion of 1.0% DKMA/KBr.

2.2.2 Dielectric characterization

The dielectric characterization of DKMA was performed using an impedance analyzer (HP model LF4192A) coupled to a temperature controlled chamber. For electrical contact, circular aluminum electrodes were placed on both sides of the sample by evaporation. The sample was heated at a 0.6°C/min rate and measures of real admittance were conducted at every 5°C in the -40 to 100°C interval. The dielectric constant (ϵ') was obtained from equation (1):

$$\epsilon' = Y'' L / (\omega A) \quad (1)$$

where L is the sample thickness, A is the metallic area, ω is the angular frequency and Y'' is the real admittance.

2.2.3 Scanning electron microscopy (SEM)

Scanning Electron Microscopy was performed using an electronic microscope (Jeol JTSM – T 330) and the samples, of 20 to 30nm thickness, were metalized using a BAL-TEC SCD 050 system, for 120s.

2.2.4 Nuclear magnetic resonance in solid state (NMR)

All solid state analyses of ^{13}C -NMR (75.4 MHz) were recorded on a Varian INOVA 300 spectrometer. The samples were packed in zirconium rotors and spun at the magic angle at 4500Hz, a relaxation delay of 6.0 s for ^{13}C respectively. All chemical shifts are reported in parts per million ppm (δ) with reference to external tetramethylsilane (TMS).

2.2.5 Thermogravimetric analysis (TGA)

The Thermogravimetric Analysis of the samples were determined using SDT 2960 Simultaneous equipment TGA (TA Instruments, Inc., New Castle, DE). The measurements were obtained using 6-11mg samples placed in alumina crucibles and heated under a continuous flow of nitrogen (50mL min^{-1}), from $10^\circ\text{C min}^{-1}$ to 1100°C .

3. RESULTS AND DISCUSSION

3.1 Vibrational Spectroscopy

Fig. 1 shows the vibrational spectrum in the infrared region of DKMA, which exhibited a broad band corresponding to the stretching vibrations of the N-H group, characteristic of amides in the region between $3700\text{-}3060\text{ cm}^{-1}$. At 2946 cm^{-1} , a characteristic band on the angular displacement of the C-H group was observed. In the region between $1880\text{-}1500\text{ cm}^{-1}$, the presence of C=O stretching bands, C=C stretching and angular deformation of NH were clearly seen. A band at 1475 cm^{-1} and another one at 1440 cm^{-1} , related to the angular displacement of the CH_2 group and to the C-N stretching, were also observed. Table 1 lists the main attributions for the DKMA [34].

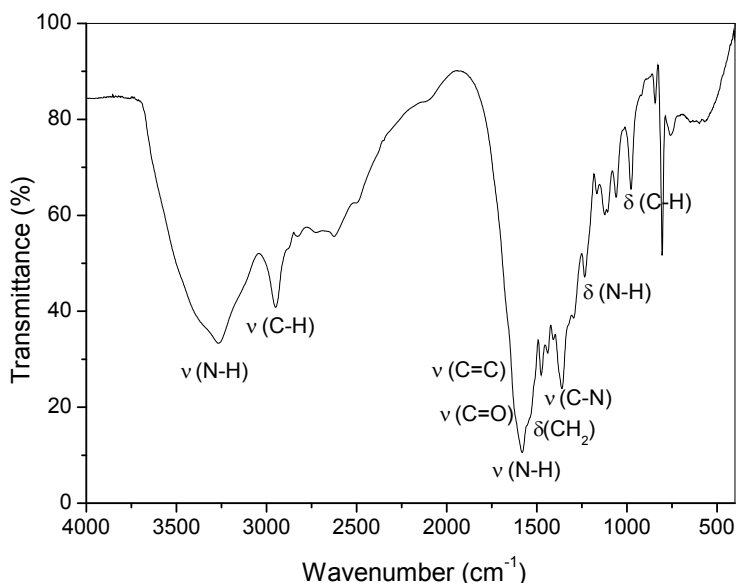


Fig. 1. Vibrational spectrum in the infrared region of DKMA

Table 1. Main vibrational attributions for DKMA found in the infrared region

Vibration type	Absorption region (cm ⁻¹)
ν (N-H)	3700 - 3060
ν (C-H)	2946
ν (C=C)	1667-1640
ν (C=O)	1640
ν (N-H)	1580
δ (CH ₂)	1475
ν (C-N)	1440
δ (N-H)	1232
δ (C-H)	972

According to the analysis of the infrared spectrum of DKMA, the formation of an amide in the reaction of DAB-Am-16 with the methyl acrylate can be observed. The primary amine groups of the starting material are converted into amides by reaction of the methacrylate (after basic hydrolysis) with the starting dendrimer material.

The molecular structure schematized in Fig. 2 was tentatively ascribed to the aforementioned compound. In the proposed structure as illustrated by Fig. 2 the carbonic chain of the methacrylate was introduced to the starting material in order to generate groups amide which can be identified by IR spectrum (Fig. 1) and ¹³C NMR solid state (Fig. 3).

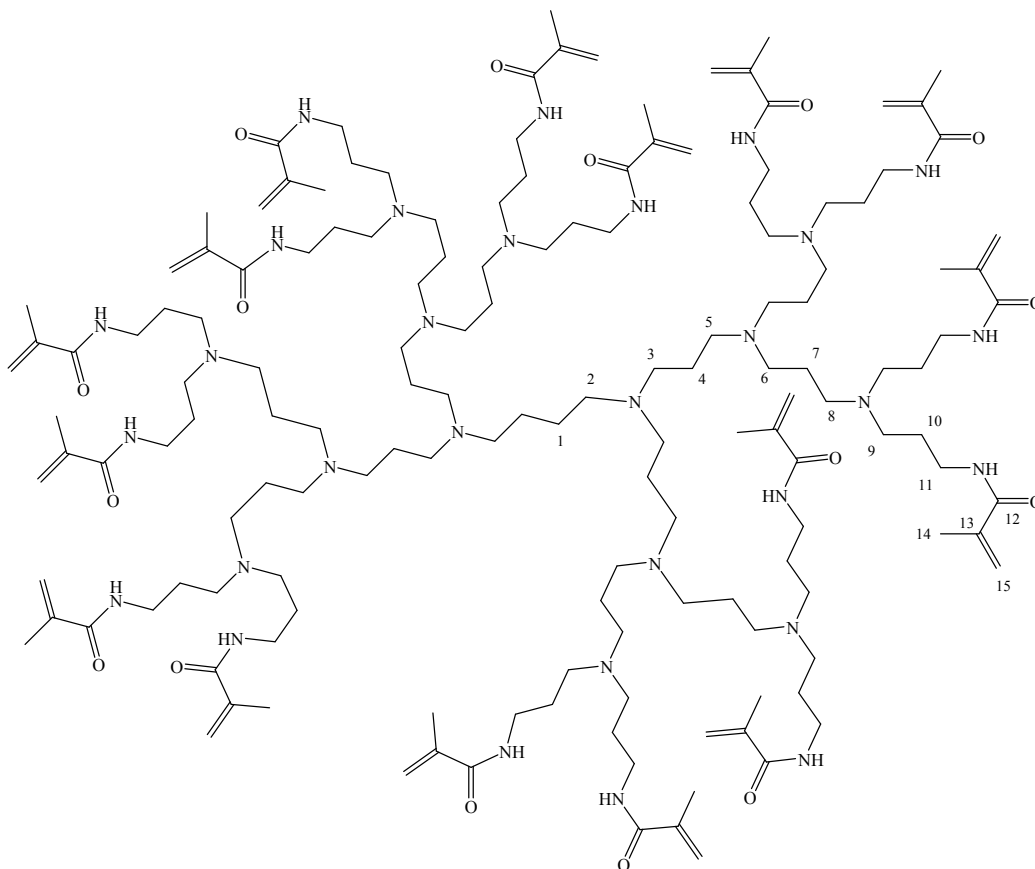


Fig. 2. Proposed scheme for the DKMA structure

In IR spectrum, as illustrated by Fig. 1, the band present in 1640 cm^{-1} is characteristic of carbonyl amide, however in methacrylate the band the carbonyl ester is in region exceeding 1700 cm^{-1} . Fig. 3 shows the spectrum of ^{13}C NMR. It is possible to observe the sign in 166.88 ppm that corresponds to carbonyl carbon (C12) of the amide group and the broad signals in $156.20\text{ -}151.02\text{ ppm}$ correspond on carbons of the double bond (C13 and C15) from the carbon chain methacrylate as well as the signal at 17.00 ppm corresponds to methyl group (C14) also from the carbon chain of the methacrylate inserted in the reaction of formation of the amide groups. The signal in 39.34 correspond to C11 bonded in N of amide group. The broad signal in the range $19.92\text{ to }23.32\text{ ppm}$ corresponds to carbons C1, C4, C5 and C10. In the range of $52.45\text{ -}56.47$ appear the signal of carbons C2, C3, C5, C6, C8, and C9 is in concordance with the ^{13}C NMR datas for dendrimer starting DAB-Am-16 [35].

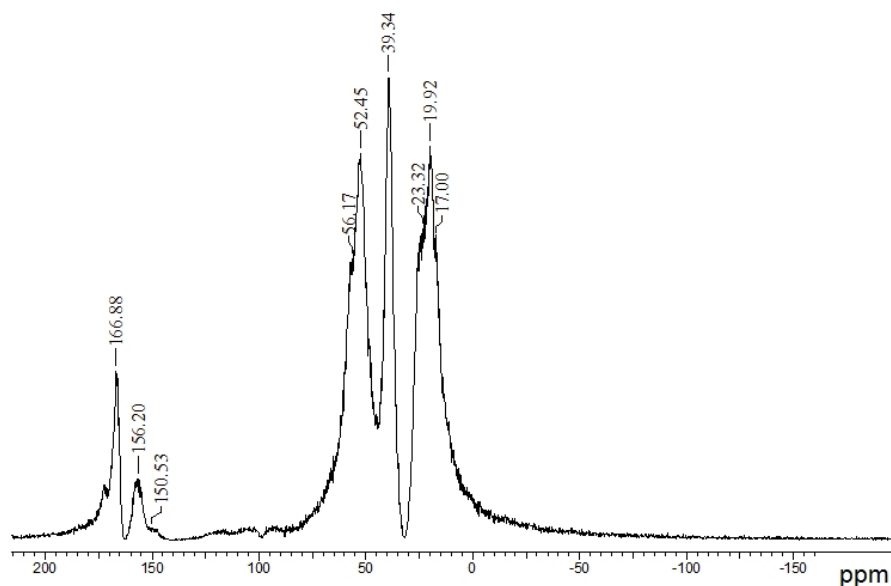


Fig. 3. ^{13}C NMR solid state for the DKMA

3.2 Dielectric Characterization

Fig. 4 illustrates the relationship of ϵ with frequency, for different temperatures. It was found that DKMA had a dielectric constant value close to the values found for the commercial polymers. It was observed that there is a slight dielectric constant decrease as a function of frequency and a significant increase with increasing temperature. The largest variations are observed from -40 to 40°C . This variation was small for higher temperatures, especially for frequencies below 100 KHz. According to the results, there was no significant variation in the dielectric constant and dielectric loss compared to the frequency range analyzed in the temperature range of -40°C to 100°C .

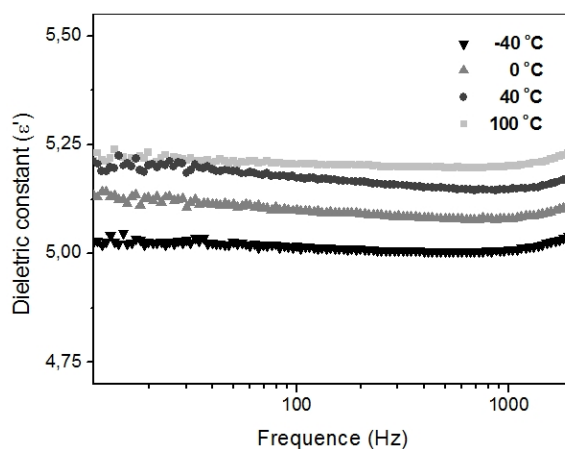


Fig. 4. Variation of dielectric constant (ϵ') as a function of frequency at different temperatures

3.3 Scanning Electron Microscopy (SEM)

Fig. 5 illustrates the SEM, on top of DKMA. Coincidentally, the material presented as an “arboreous” shape with a collapsed conformation very close to that presented by theoretical studies, in which the dendrimer is prepared in a basic medium (high pH). According to the literature [36], if the synthesis were carried out at a low pH, the interior of the tertiary amine groups would be protonated, hence leading to the repulsion of charges, and this repulsion of charges would lead to an extended conformation of the dendrimer. Note that the dendrimer was prepared in a basic medium (KOH), in order to facilitate the formation of the primary amide.

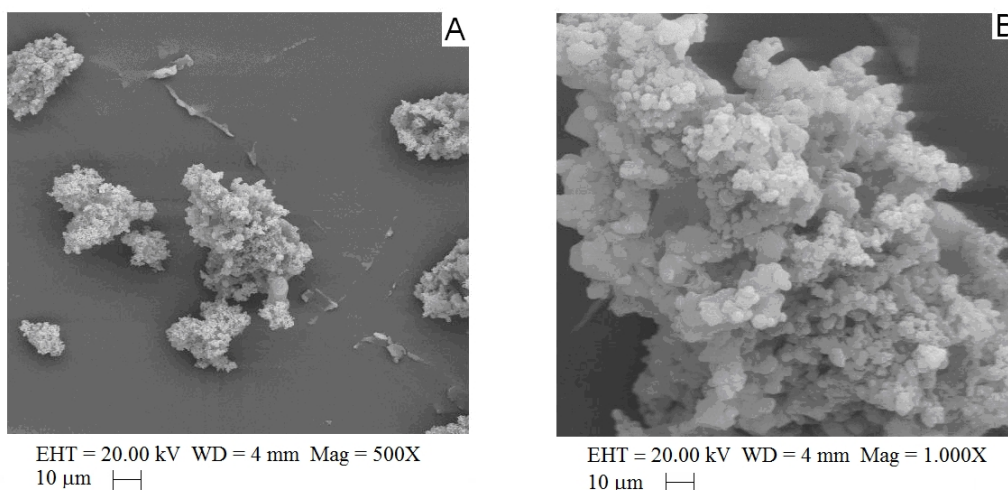


Fig. 5. Scanning electron microscopy of DKMA: Increase of 500 x (A); Increase 1000x (B)

3.4 Thermogravimetric Analysis

Fig. 6 depicts the analysis of the thermogravimetric curve of DKMA. The analyses were obtained under nitrogen atmosphere. The thermogravimetric curve gives an indication on the thermal stability of the material regarding continuous heating. For the TG of DKMA under N_2 atmosphere, three stages of mass loss were observed, the first one from room temperature to $126^\circ C$ (12.22%) the second one from 126 to $628^\circ C$ (64.85%) and the third one from 628 to $1100^\circ C$ (21.12%). The first stage was ascribed to the elimination of physically adsorbed water molecules, the second stage refers to the elimination and total decomposition of organic compounds [37] (propylimine groups) and the third one, a slower decomposition, was ascribed to decomposition of the peripheral groups containing the $H_2C=CH-CO-NH$ -connection type. Thus, we come to the conclusion that the thermal stability of the modified dendrimer depends on the distribution of peripheral groups containing amide bonds of the $H_2C=CH-CO-NH$ - type.

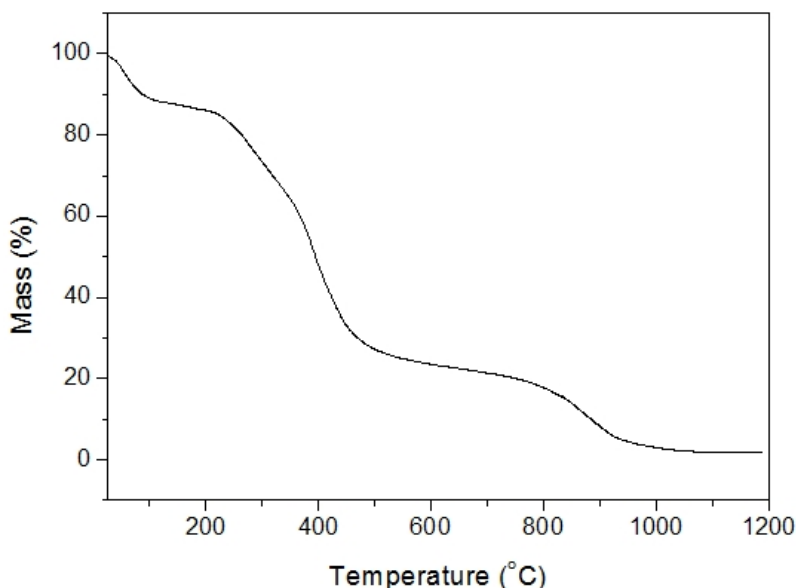


Fig. 6. Thermogravimetric curve of DKMA (nitrogen atmosphere)

4. CONCLUSIONS

The DAB-Am-16 dendrimer (G3) modified with methyl acrylate was characterized by elemental analysis, vibrational spectroscopy (FT-IR), thermogravimetry and scanning electron microscope. The modified dendrimer behaved as an organic insulator with a dielectric constant very close to the silicon-based compounds. The electron microscopy indicated that the modified dendrimer presented a collapsed shape, expected by the proposed synthesis route. These data are relevant, given that there is no report on any electrical properties of analog dendrimers in the literature.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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